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# Synthesis and Characterization of A New Class of Thermosetting Resins: Allyl and Propargyl Substituted Cyclopentadiene Derivatives

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## ABSTRACT

A series of all-hydrocarbon resins were synthesized by reacting cyclopentadiene with allyl chloride, propargyl chloride, or a mixture of allyl chloride and propargyl chloride, under phase transfer conditions. Phase transfer reactions with and without added solvents, and with either quaternary ammonium or crown ether type catalysts, yielded similar products consisting of a mixture of 1,1-disubstituted cyclopentadiene (minor amount) and 2-3 isomers each of tri-, tetra-, penta- and hexa-substituted derivatives. No further reaction of each these components was possible. The overall substitution pattern varied little with changes in reaction conditions although limiting the allyl chloride content led to still reactive, partially substituted products. Incorporation of all-propargyl and high propargyl-to-allyl mixed functionalities on cyclopentadiene yielded products whose stability was very low, hindering their thorough characterization. Preliminary evaluation was therefore carried out for mixed resins with lower propargyl functionality. The allyl substituted resin (allylated cyclopentadiene, ACP) underwent thermal cure (without initiator) at around 200 °C while allyl/propargyl substituted resin (7:1 ratio, APCP) showed a faster, lower temperature cure at around 120 °C. Cationic cure of ACP was also

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initiated by a novel sulfonium salt at around 100 °C.

Neat ACP resin when cured at 200 °C gave material with a flexural storage modulus value of about 300 MPa. Further cure at 250 °C raised the modulus to 1.2 GPa. This resin gave composites with excellent properties when used with glass and carbon fibers. Flexural modulus values (by DMA) of ca 66 GPa were obtained for ACP/carbon fiber composites compared to 42 GPa for epoxy/carbon composites made in our laboratories using commercially available materials. The modulus values at 300 °C dropped to 10% of the room temperature value for the epoxy composites, while the ACP/carbon composite maintained 60% of its room temperature value at 300 °C. When brought back to ambient temperature, the moduli of the latter samples had increased to 80 GPa and those of the epoxy composites dropped to 23 GPa. Glass fiber ACP composites performed similar to an epoxy composite up to 200 °C but maintained properties up to 300 °C while those of the epoxy were drastically reduced. TGA analysis of both cured ACP resin and its composites showed decomposition beginning at 375 °C. Three-point bending tests indicated very high modulus with brittle failure for ACP composites. Scanning electron micrographs showed moderate bonding of the new resin to both carbon and glass fiber surfaces. This new class of thermosetting resins offers excellent potential for application in low-cost glass and carbon composites with good thermal and physical properties.

## INTRODUCTION

All-hydrocarbon thermosetting resins (such as those based on polybutadiene) (1) make possible composites with excellent electrical properties (low dielectric constant) and

chemical resistance. Such resins offer a distinct advantage over polyester and epoxy materials through increased resistance to attack by acids and bases. In addition, their inherent hydrophobicity provides enhanced hot-wet stability and long-term resistance to humidity and saline environments. These unique properties are ideal for sonar and radome application, for example, and could lead to replacements for traditional glass fiber reinforced composites in the marine industry. However, problems do exist with currently available candidates. While polybutadiene resins offer better hydrolytic and high-temperature mechanical properties than epoxies, their room temperature mechanical properties are inferior. Post-curing (with further crosslinking) can improve the low temperature properties while the incorporation of co-reactive monomers such as triallyl cyanurate epoxies increases mechanical properties. However, introduction of polar groups decreases solvent resistance and complicates the basic resin composition and cure chemistry. Resins based on dicyclopentadiene also are not suitable for high temperature applications due to low  $T_g$  (2). Other hydrocarbon resins such as benzocyclobutene-containing materials can be used at high temperatures and possess excellent dielectric properties but at very high cost (3).

Substitution reactions on cyclopentadiene have led to a wide variety of materials from bismaleimide resins to transition metal complexes (4),(5),(6). Multiple substitutions can be achieved under basic conditions using a variety of reactants from acrylonitrile to t-butyl chloride (7),(8),(9). Reactions involving alkyl chlorides have been reported to yield a mixture of multiply substituted derivatives in various isomeric forms (7). Similar products have been reported from base-catalyzed alkylation of cyclopentadiene with

primary and secondary alcohols at 200 °C (10),(11). Previous work on methylation of cyclopentadiene has shown that the structures of the substituted products obtained depend mainly on the character of the substituent and not on the method of synthesis (12). We have established that the substitution reaction on cyclopentadiene with acrylonitrile can go to completion with six substitutions on each ring (13). This opens up possibilities for new reactive materials with high functionality and low viscosity.

The cyclopentadiene reaction continues to high degrees of substitution on the ring due to the directing effect of substituents for incoming electrophiles. In the case of methyl iodide as the electrophile, when a methyl group is already present on the ring, the order of positional selectivity is  $\beta > \gamma > \alpha$  with the attack at  $\beta$  being 3.5 times greater than attack at  $\gamma$ , while the  $\alpha$  position is the least susceptible (14). This suggests that polyalkylation with allyl chloride and propargyl chloride should lead to multiple substitution on the cyclopentadiene ring and thus give highly functionalized materials. In fact, singly allyl substituted cyclopentadiene has been synthesized and used to make a new class of thermosetting resin based on allylnadimide (4),(15). In our work, we have readily functionalized cyclopentadiene with multiple allyl and/or propargyl groups. The allylated cyclopentadiene (ACP) resin was evaluated as a matrix resin for both glass and carbon fiber composites. In this paper, we discuss the synthesis of these resins, their cure evaluation using DSC and FT-IR, and the properties of the neat resin along with those of composites containing glass and carbon fibers.

## EXPERIMENTAL

Dicyclopentadiene was obtained from Aldrich Chemical Company and cracked to

cyclopentadiene at 175 °C with a 30" Vigreux column. Allyl chloride, propargyl chloride, Aliquat 336 (a quaternary ammonium phase transfer catalyst), p-cresol, 1-bromodecane, N-bromosuccinimide, NaSbF<sub>6</sub>, and tetrahydrothiophene were obtained from Aldrich Chemical Company and used without further purification. All solvents were used as obtained from Fisher or Aldrich. AS-4 unsized carbon fibers were donated by Hercules Chemical Company and vinyl silane treated glass fibers were donated by Owens Corning Fiberglass Company. Composites were made using a mold that gave samples 60 mm long and 12.7 mm wide with variable thickness.

Cure analysis was investigated using a Perkin-Elmer DSC 7 differential scanning calorimeter. IR spectra were collected on a Perkin-Elmer 1600 FT-IR. Solution <sup>13</sup>C NMR spectra were obtained on a Bruker AC-200 spectrometer. A DuPont 9900 data station equipped with dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) modules was used for thermo-mechanical analysis. Three-point bending tests were carried on a Materials Testing System (MTS) mechanical analyzer with a sample length-to-thickness ratio of 16 and a traverse speed of 2 mm/min. Scanning electron micrographs (SEM) were obtained with an Electroscan environmental scanning electron microscope.

#### **Synthesis of Allylated Cyclopentadiene (ACP)**

The general reaction scheme for synthesis of allylated cyclopentadiene and propargylated cyclopentadiene is given in Figure 1. Cyclopentadiene (5 g, 0.075 mol) was cooled to 15 °C in an ice water bath. KOH (85 g, 1.5 mol) was added as a 50% (w/w) solution in water. Aliquat 336 (0.75 g, ca 2 mol-% based on cyclopentadiene) was

added to this mixture. This mixture was mechanically stirred for 15 min during which the solution turned yellow; longer reaction time gave a pink color probably due to a high concentration of cyclopentadienyl anion. Allyl chloride (46 g, 0.6 mol) was added over a period of 2 h during which the solution turned dark pink in color. If addition of allyl chloride is not well controlled, the heat liberated will lead to side reactions such as dimerization of cyclopentadiene and evaporation of cyclopentadiene and allyl chloride. The ice water bath was then removed and the reaction mixture was stirred for 6 h at room temperature. The reaction was monitored by gas chromatography until there was no change in the composition of reaction products. This procedure has been used for large scale reaction (up to 80 g) of cyclopentadiene in which case the addition of allyl chloride took about four hours.

The aqueous phase was separated and the organic phase was neutralized with dilute HCl. The organic phase was then washed with a 50/50 mixture of water/methanol to remove the phase transfer catalyst; higher methanol to water ratios make the removal of Aliquat 336 easier but with loss of some product. Complete removal of Aliquat 336 can be achieved by passing the product mixture through silica gel (60-200 mesh). The methanol used for extraction was rotary evaporated. The yield of the final mixture was 18.0 g. It contained products with 2 to 6 allyl substituents in the ratios 9, 11, 20, 30 and 30%, respectively, by GC analysis. Yield calculated based on cyclopentadiene (using all degrees of substitution) was close to 100%. The excess allyl chloride recovered from the reaction can be recycled. Increasing the reaction temperature after initial room temperature reaction did not influence the ratio of products. Reactions in the presence

of organic solvent (hexane, benzene or toluene) with Aliquat 336 as catalyst or without organic solvent and with crown ether as catalyst, proceeded slowly but resulted in the same product composition.

#### **Synthesis of Propargyl (PCP) and Allyl/Propargyl (APCP) Substituted Cyclopentadienes**

Reacting cyclopentadiene with propargyl and allyl/propargyl mixtures was carried out with the procedure used for allyl incorporation. The feed ratios of allyl chloride to propargyl chloride chosen were 1:1, 3:1 and 7:1 for the allyl/propargyl mixtures. Resin with higher amounts of propargyl groups showed reduced stability during and after work up, and substitution with propargyl chloride alone (PCP) resulted in a material that gelled in the process of work up indicating low shelf life but high reactivity. Resin with a 7:1 feed ratio was stable enough for further thermal and FT-IR analysis. The synthetic procedure involved mixing cyclopentadiene (3.0 g, 0.045 mol), 50 % aqueous KOH (50.0 g, 0.89 mol) and Aliquat 336 (0.4 g, 0.8 mmol) in a 3-necked round-bottom flask cooled to 15 °C equipped with a mechanical stirrer. An allyl chloride and propargyl chloride mixture (3.5 and 24.0 g, respectively; ca 7:1 mol feed ratio) was added over a period of 1 h. The reaction temperature was then allowed to reach ambient and the mixture stirred for another 6 h. The aqueous phase was separated and the organic phase was neutralized with dilute HCl. The organic phase was then washed with a 50/50 mixture of water/methanol to remove the phase transfer catalyst. Rotary evaporation of the organic phase resulted in a dark brown APCP-7:1 resin. Resin APCP-3:1 was obtained in the same way but was not studied extensively. The yields of these resins were significantly lower (30-50%) than ACP due to crosslinking during work up.

### **1-(p-Decyloxybenzyl)tetrahydrothiophenium hexafluoroantimonate (DTHA)**

For cationic curing, 1-(p-decyloxybenzyl)tetrahydrothiophenium hexafluoroantimonate (DTHA) was synthesized according to the scheme given in Figure 2. p-Cresol (8.6 g, 79.5 mmol), 1-bromodecane (19.35 g, 87.5 mmol) and NaOH (4.77 g, 120 mmol) were mixed in 50 ml of ethanol. The solution was refluxed for 5 h. GC analysis showed complete conversion of p-cresol to p-decyloxytoluene which was purified by distillation to give 14.2 g (yield 72%). p-Decyloxytoluene (5 g, 20 mmol) and one equivalent of N-bromosuccinimide (NBS, 3.6 g, 20 mmol) were dissolved in 50 ml of benzene. To this was added 0.2 g of AIBN and the solution was refluxed for 12 h. The reaction mixture was extracted with water to remove succinimide and unreacted NBS. The benzene solution was concentrated and tetrahydrothiophene (1.8 g, 20.5 mmol) was added. A precipitate formed immediately that was filtered and washed with cold hexanes and ethyl ether; yield 2.7 g, 33%. To 1 g of this salt dissolved in 1-butanol was added 1 g of NaSbF<sub>6</sub> in 2 ml of water to give an immediate white precipitate. This material was filtered, washed with water and ethyl ether, and recrystallized from ethanol to give DTHA (0.93 g, 73%).

### **Composite Formation**

A stainless steel mold was used with cavity dimensions of 60 mm by 12.7 mm. The mold surfaces were sprayed with Fluoroglide® to facilitate easy removal of the composite sample. ACP composites were formed by sequentially laying bundles of fibers in the mold cavity and wetting the fibers with ACP resin. The fibers were spread out to facilitate mixing between bundles (otherwise the composites split into bundles when taken

out of the mold). This process was continued till the necessary thickness was obtained in the final composite (ca 2 mm). The top load was placed in the cavity to squeeze out excess resin. Samples were cured for 6 h each at 200 °C and 250 °C without added initiator. This technique results in composites with unidirectionally oriented fibers.

ACP resin was mixed with 0.5% of DTHA as initiator for cationic cure and used as matrix material for ACP/glass composites. Glass fiber composites were cured for 6 h each at 120 °C and 200 °C. Post-curing was then carried out on glass fiber composites at 250 °C. Control samples were made from Epon-828/MDA (methylene dianiline) under standard curing conditions(16). The resin contents of the composites were determined from weight difference between final composite sample and weight of fibers used. Resins containing propargyl functionalities have not been evaluated for composite application.

## RESULTS AND DISCUSSION

### Resin and Initiator Synthesis

The reaction of cyclopentadiene and allyl chloride was monitored by gas chromatography. Increase in the high-retention-time products was observed for times up to 6 hours at room temperature after which there was no further change in the composition. The <sup>13</sup>C NMR spectrum of ACP (Figure 3, top trace) indicates a complex mixture of products with multiplets for all the ring and allyl carbons. The sets of peaks at 115 and 135 ppm correspond to the vinyl group carbons of the allyl functionality. The multiple peaks confirm formation of products with different degrees of substitution and with different isomer structures. The peaks between 50 and 60 ppm come from the saturated quaternary carbons on the cyclopentadiene ring arising from disubstitution (two

allyl groups on the same carbon). The methylene units of the allyl groups also have two sets of peaks (around 30 and 40 ppm) depending on whether the allyl group is attached to a saturated or unsaturated carbon of the cyclopentadiene ring.

High degrees of substitution on cyclopentadiene resulted in this reaction due to a combination of favorable and unfavorable conditions. First, as the reaction proceeds, a second substitution on the same carbon of cyclopentadiene (which terminates the reaction) is unfavorable due to steric inhibition and the distribution of electronic charges on the carbons (higher charges on  $\beta$  and  $\gamma$  positions making them more reactive than  $\alpha$ ). This favors more highly substituted derivatives. On the other hand, with the reaction conditions used here involving very high concentrations of allyl chloride, termination occurs in greater amounts than that reported for polymethylation (14). To confirm product identities, we have isolated the lowest boiling component, 1,1-diallylcyclopentadiene, by vacuum distillation. The structure of this material was clear from its  $^{13}\text{C}$  NMR spectrum (Figure 3, bottom trace). Due to the symmetry of the molecule, there are only six unique carbons (two saturated and four unsaturated). The methylene units of the allyl groups appear around 38 ppm, the quaternary carbon of the ring at 60 ppm and all unsaturated carbons between 110-150 ppm. The gas chromatograph of this compound gave a single retention time corresponding to the lowest retention time of the mixture.

The FT-IR spectra of ACP and APCP resins are given in Figure 4. ACP was identified with the allyl group C-H out of plane bending at 994 and 908  $\text{cm}^{-1}$ , unsaturated C-H stretching at 3076  $\text{cm}^{-1}$  for the allyl groups and 3012 and 2976  $\text{cm}^{-1}$  for the cyclopentadiene C-H groups (top trace of Figure 4). The C=C stretching was also

observed at 1640 cm<sup>-1</sup>. Allyl/propargyl substituted cyclopentadienes were characterized by FT-IR for quantitation of the amount of allyl and propargyl groups incorporated into the resin. To quantitate, a calibration plot was made for the area corresponding to the C-H stretching of the allyl and propargyl groups by mixing known amounts of allyl chloride and propargyl chloride. In the APCP resins, the C-H stretching at 3303 cm<sup>-1</sup> and triple bond stretching at 2124 cm<sup>-1</sup> were observed due to the propargyl groups in addition to the stretching frequencies corresponding to the allyl and cyclopentadiene groups,. The C-H stretching at 3303 cm<sup>-1</sup> decreased with the increase in the allyl:propargyl ratio from 3:1 to 7:1 in the feed. Analysis of the resins using the calibration plot for known mixtures of allyl and propargyl chloride indicated that allyl chloride was reacting at a higher ratio than was in the feed. With a 7:1 allyl:propargyl chloride feed ratio, the substitution ratio in the product was found to be 10:1. Substitution of cyclopentadiene with allyl chloride carried out in the presence of organic solvents such as mixed hexanes or benzene yielded product ratios similar to product obtained without solvent. Replacing quaternary ammonium salts with crown ether catalysts required longer reaction times to give the same product composition.

The cationic curing agent that we synthesized is a structurally modified version of those reported (17) to improve solubility in the resin. <sup>13</sup>C NMR spectra of the reactants, intermediates and product (DTHA) are given in Figure 5. The presence of the ether group in reagent 1 (refer to Figure 2) was confirmed by the peak at 70 ppm (Figure 5, top trace). The conversion of the toluene methyl group to bromomethyl group was confirmed by disappearance of the peak at 22 ppm and appearance of a new peak at 44 ppm

(Figure 5, middle trace). Conversion of the bromomethyl group to the sulfonium salt was also confirmed by changes in chemical shift for this methylene unit from 44 ppm to 60 ppm (Figure 5, bottom trace). The exchange of bromine anion with hexafluoroantimonate was indicated by FT-IR observation of a peak at  $660\text{ cm}^{-1}$  (for  $\text{SbF}_6^-$ ).

### **Cure Evaluation of ACP and APCP**

Two modes of cure were evaluated for ACP resin, thermal cure and cationic cure with the sulfonium salt initiator. DSC analysis of thermal cure without added initiator gave an exotherm maximum at around  $200\text{ }^\circ\text{C}$  (Figure 6, top trace). The DSC thermogram of ACP cured with DTHA (0.5 wt-%) gave an exotherm at  $120\text{ }^\circ\text{C}$  followed by an exotherm at  $250\text{ }^\circ\text{C}$  (middle trace). This high temperature post-cure at  $250\text{ }^\circ\text{C}$  was confirmed by taking a sample up to  $120\text{ }^\circ\text{C}$ , cooling back to room temperature and heating back up past  $250\text{ }^\circ\text{C}$  (bottom trace, enlarged along y axis). The second run on these samples did not show further cure or any glass transition temperature as expected for high crosslink density materials.

DSC thermograms of the APCP resins showed two exotherms when cured without added initiator (Figure 7). The low temperature exotherm at around  $120\text{ }^\circ\text{C}$  in APCP-7:1 (Figure 7, middle trace) was not observed in the thermal cure of ACP without initiator (Figure 7, top trace). This is attributed to the cure of the propargyl groups as the intensity of this exotherm is lowered for the APCP-3:1 resin (Figure 7, bottom trace).

### **Spectroscopic Characterization of Thermal Cure**

The FT-IR spectra of ACP cured at different temperatures are given in Figure 8. The spectrum of resin cured at  $200\text{ }^\circ\text{C}$  showed incomplete conversion as indicated by the

presence of allyl bands at 908, 994, 1560, and 3076 cm<sup>-1</sup> (middle trace). Further cure at 250 °C led to complete conversion of the allyl groups as shown by disappearance of these bands. In addition, a new peak was seen at 1650 cm<sup>-1</sup> resulting from oxidation to give C=O groups during cure carried out in air. Similar FT-IR analysis of cationically cured ACP resin showed incomplete cure at 120 °C and complete cure at 250 °C. FT-IR spectra of the mixed allyl and propargyl functionalities (APCP-7:1) showed both propargyl and allyl groups disappearing slowly with temperature up to 250 °C (Figure 9, peaks at 3300 and 3076 cm<sup>-1</sup>) (18). The C-H stretching band at 3300 cm<sup>-1</sup> reduced at a faster rate compared to the 3076 cm<sup>-1</sup> band, indicating faster cure of the propargyl groups. At 250 °C, the propargyl groups were completely absent, whereas the allyl groups were still present in small amounts.

#### **Physical Properties of Cured ACP**

The DMA for neat ACP resin cured at 200 °C possesses a room temperature flexural modulus of 450 MPa. The same sample further cured at 250 °C showed an increase in modulus to 1.3 GPa. This increase is associated with continuation of cure at 250°C as was seen by DSC and FT-IR analysis. The sample cured at 250 °C maitained a 0.6 GPa modulus up to 200 °C. A room temperature flexural modulus value of 1.2 GPa is comparable to commercial epoxy resins. However, since the specific gravity of the new cured resin (very close to 1.0) is lower than that of the cured epoxy (1.2) (19), the *specific* modulus is even better for ACP resin. Thermogravimetric analysis of ACP at 10 °C/min in air showed decomposition beginning around 375 °C. TGA analysis carried out on samples with various cure histories showed no significant differences in decomposition

pattern.

### Properties of ACP Composites

All carbon/ACP composites in this study contained about 30% resin by weight. Room temperature flexural modulus values were much higher for these materials compared to control samples made from Epon-828/MDA. Flexural modulus values at 275 °C of ACP/carbon composites were very close to the room temperature modulus values of the epoxy composite (Figure 10). The advantage of ACP resin over epoxies was clearly seen in the second run on the same samples. Due to continued cure of ACP resin, the room temperature modulus value increased from 66 to 81 GPa while that of the epoxy composite dropped from 40 to 22 GPa. This indicates the potential of the ACP resin in higher temperature, higher performance applications.

ACP is also an excellent candidate for glass fiber composites due its low cost and good thermo-mechanical properties. Glass/ACP composites were made with about 30% resin by weight. The flexural modulus values for glass/Epon-828/MDA system and glass/ACP composites (both cured under comparable conditions) were in the same range (20-25 GPa, Figure 11). However, ACP again provides improved properties above 200 °C compared to Epon-828/MDA composites (18 versus 11 GPa at 200 °C). Second-run DMA data confirmed that glass/ACP samples maintained modulus values of 19 GPa up to 350 °C. This improved thermal behavior suggests applications where traditional epoxy-glass fiber composites are unable to maintain properties.

The all-hydrocarbon nature of ACP resin also provides excellent moisture resistance. DMA testing of both Epon-828 and ACP glass fiber composites was done

before and after submersion in boiling water for 24 hours. The epoxy composites showed loss of property at temperatures up to 100°C due to water absorption causing plasticization (Figure 12). Once the absorbed water was driven off, however, the samples regained their initial modulus values. Such poor hot-wet strength behavior is commonly observed for epoxy composites (20) and is even worse for extended exposure which causes hydrolysis. In contrast, glass/ACP composites did not show any reduction in DMA properties after water treatment (Figure 12). We are extending the short-term water tests to more completely evaluate the effect of moisture on gradual loss of interfacial adhesion similar to studies carried out on epoxy systems (21). If sustained in longer tests, the excellent moisture resistance of ACP resin seen so far should eliminate or greatly reduce the problems of reversible water absorption and interface degradation seen for epoxy composites.

Three point bending test results for the carbon/ACP and glass/ACP composites tested perpendicular to the fiber orientation are given in Figure 13. The modulus of the carbon/ACP systems was higher than the glass/ACP composite due to better mechanical properties of the carbon fibers. In both cases brittle failure occurred with very low energy to break. This is in agreement with presumed high crosslink density resulting from the high functionality of ACP resin. For comparison, the stress-strain curve of glass-Epon-828/MDA composite is also given in Figure 13. The ACP resin showed higher modulus than the epoxy system but failed more abruptly. The toughness of the ACP composite is therefore less than that of the Epon-828/MDA composite.

Scanning electron micrographs of carbon composites cured at 250 °C and fractured

in the three-point bending test showed moderate adhesion of resin to unsized carbon fibers, indicating matrix-limited properties in this test direction (Figure 14). SEM analysis of the ACP resin-glass fiber composites also showed moderate adhesion of resin to the vinyl silane treated glass fibers after transverse fracture (22).

### **Conclusions**

All-hydrocarbon resins were synthesized through substitution reaction on cyclopentadiene with allyl and propargyl groups. Resins with high average functionality were obtained. Incorporation of propargyl groups yielded products that underwent faster cure and possessed low shelf life. Cure of the ACP resin was achieved with and without cationic curing agent. Thermal cure without initiator required temperatures of 200-250 °C while the presence of the sulfonium salt initiator allowed the initial cure temperature to be reduced to 110 °C. Flexural modulus values were better for ACP resin than Epon-828/MDA with carbon fiber reinforcement at all temperatures up to decomposition. With glass fibers, ambient temperature properties were comparable to those of the epoxy composites although at temperatures above 200 °C, the ACP composites performed markedly better, especially at temperatures approaching 300 °C. Three-point bending results indicated that the ACP resin had higher modulus but lower toughness compared to the epoxy resin. Preliminary boiling water experiments indicate that the ACP/glass composites did not show deterioration in mechanical properties.

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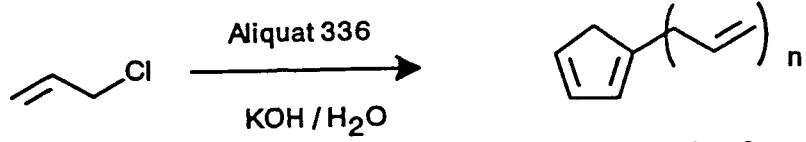
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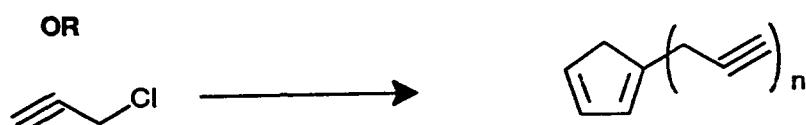
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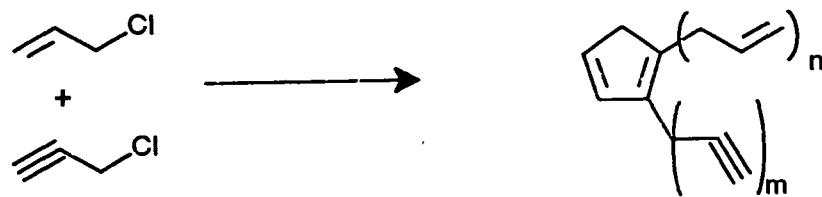
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where  $n = 2$  to 6

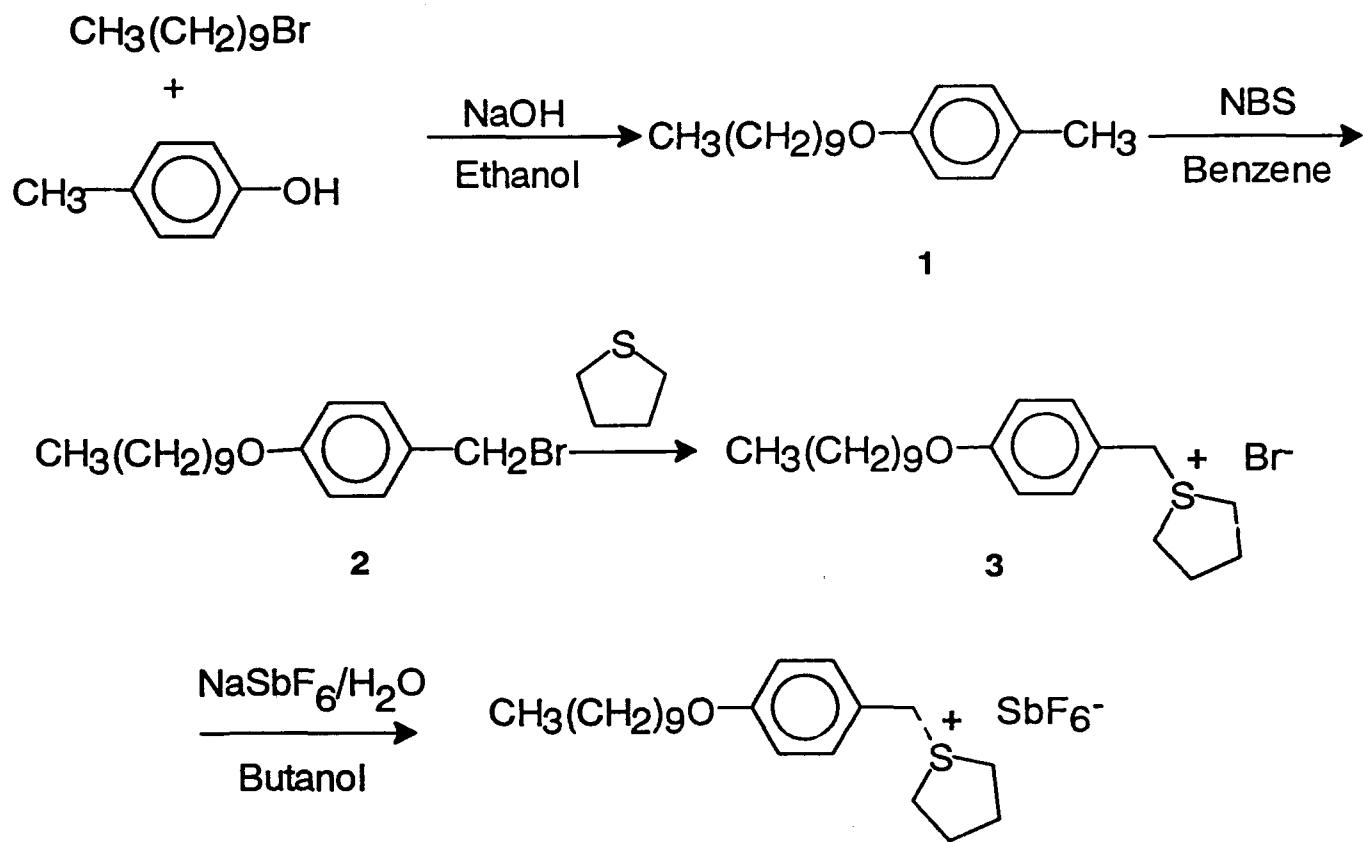


where  $n = 2$  to 6

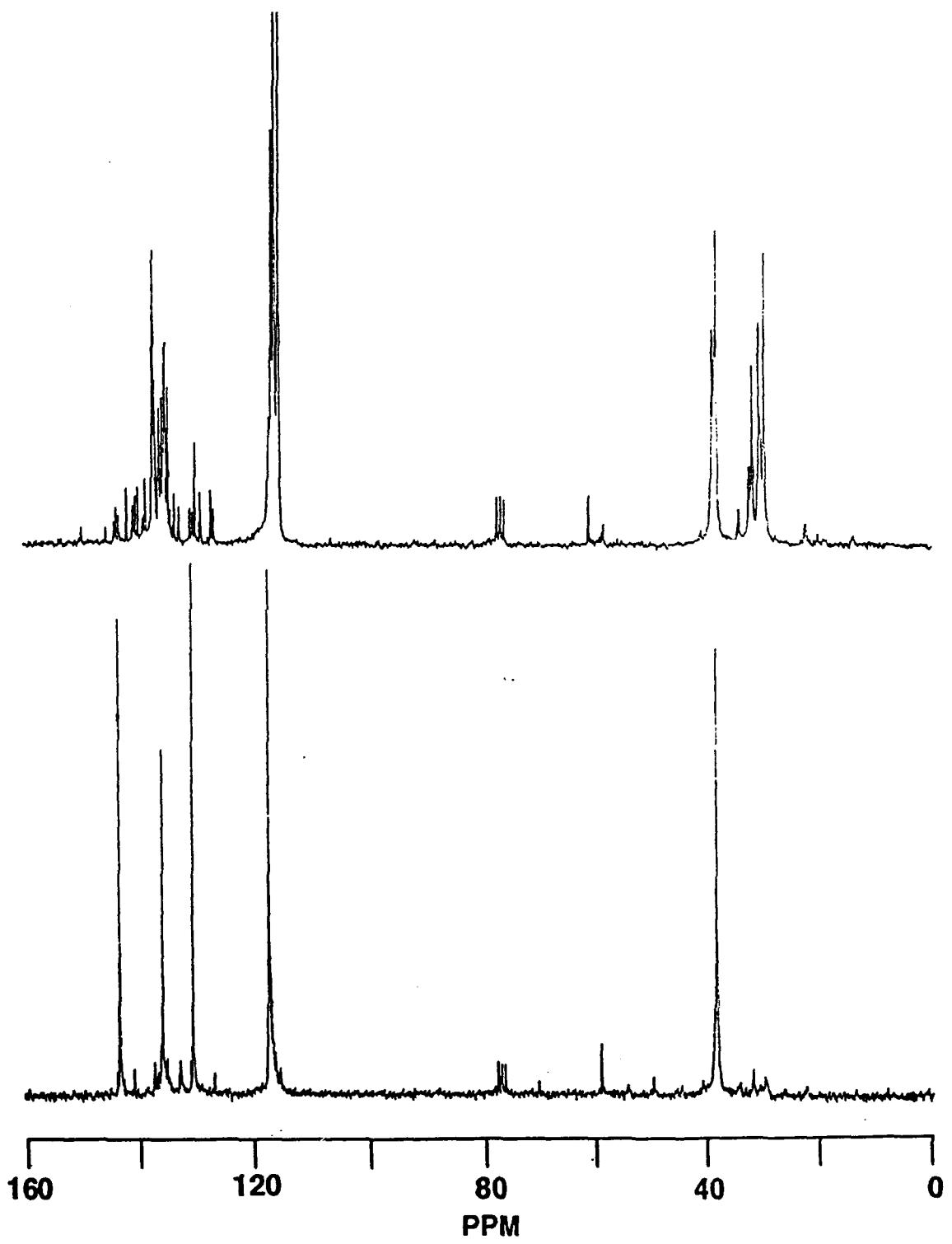


where  $n+m = 2$  to 6

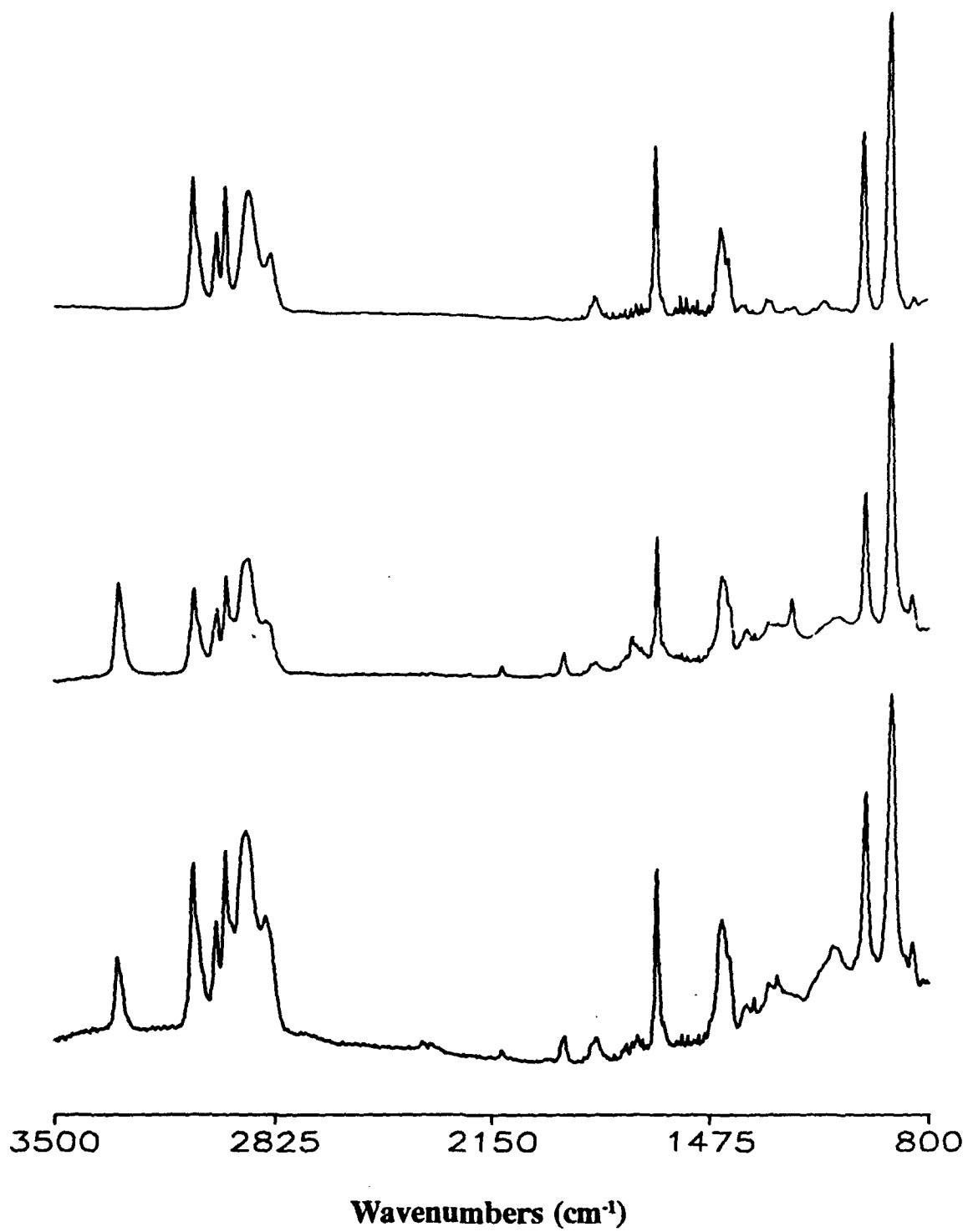
Mathews Fig 1



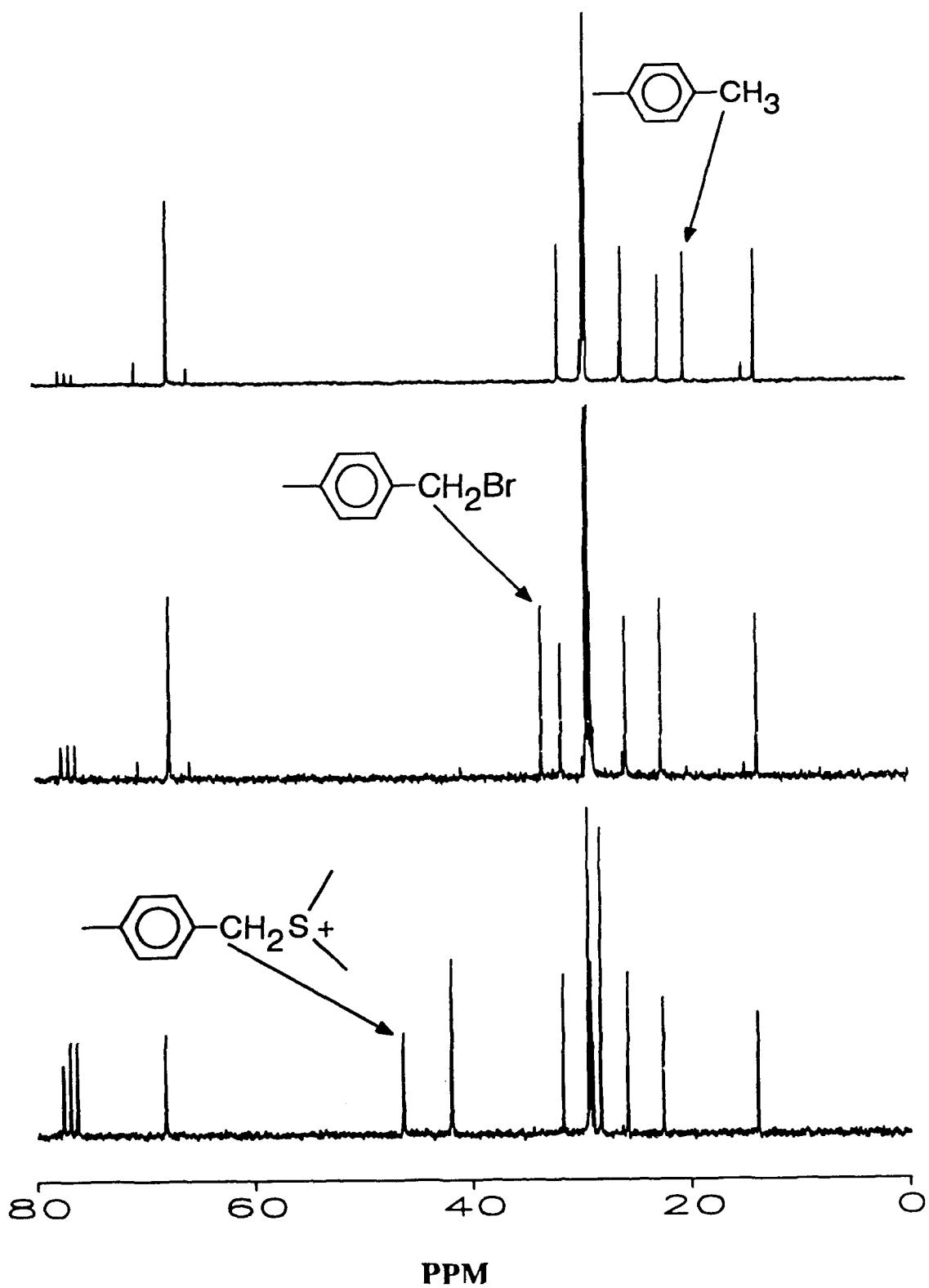
mathias Fig 2



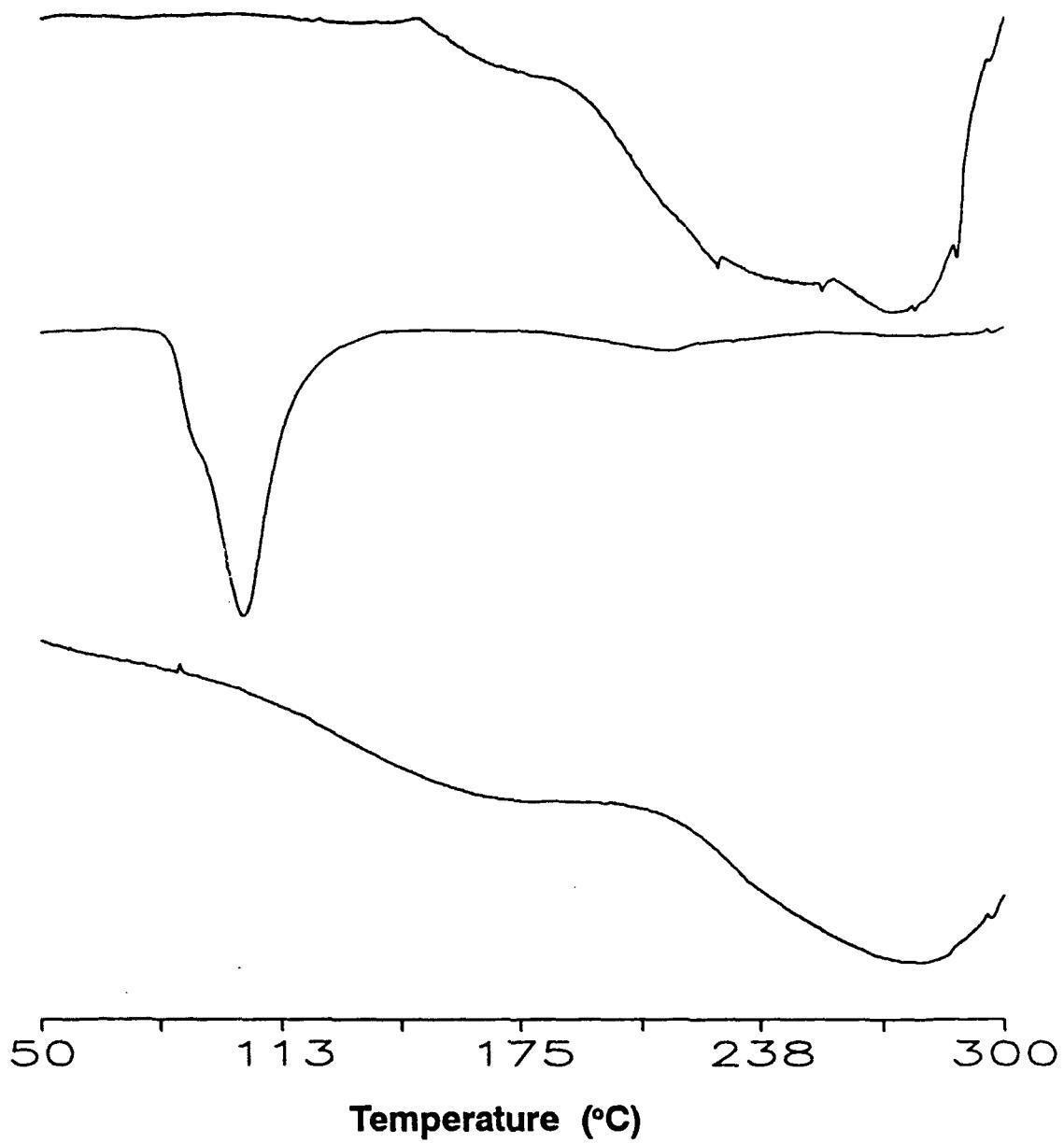
Mathias Fig 3



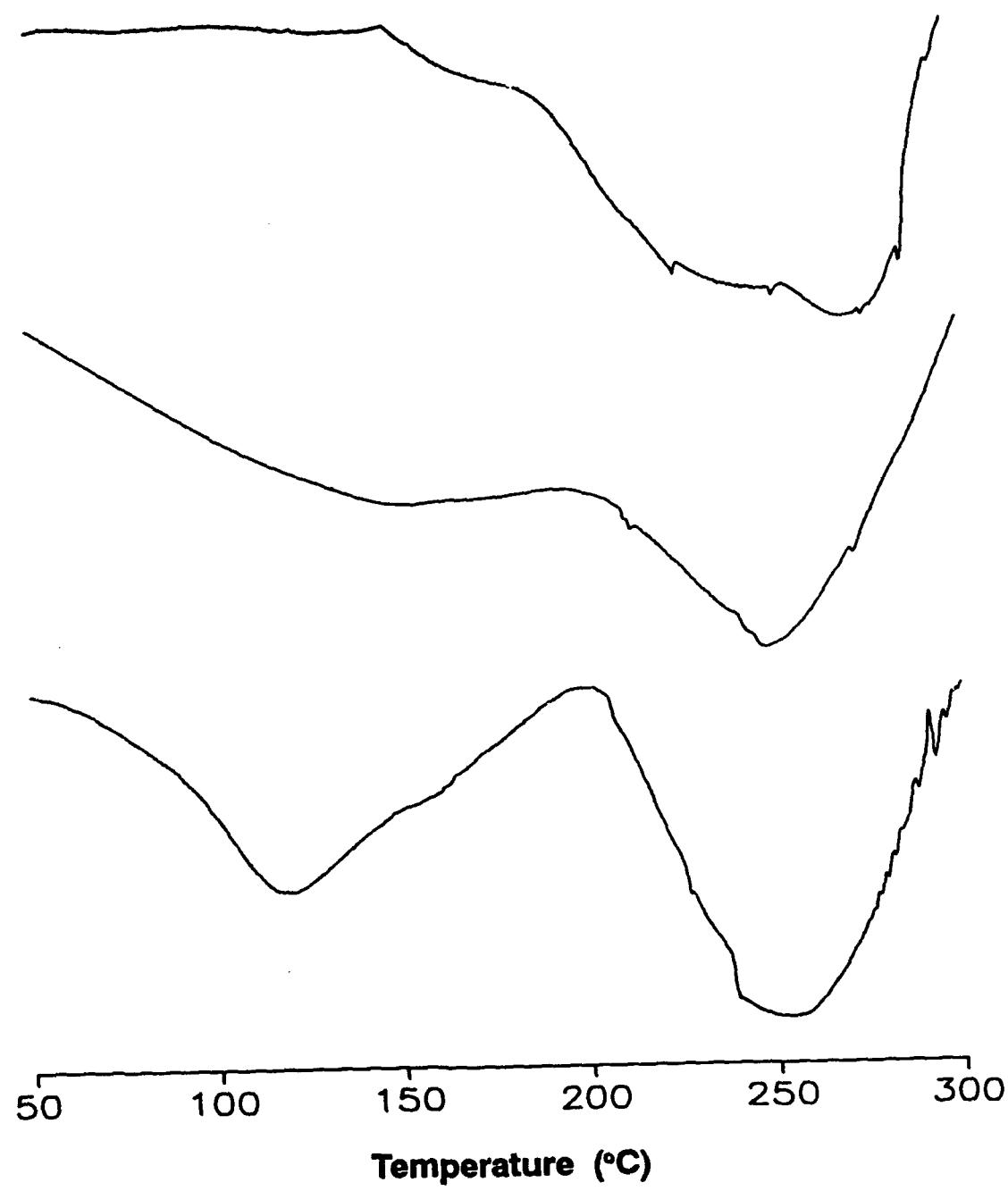
mathias Fig 4



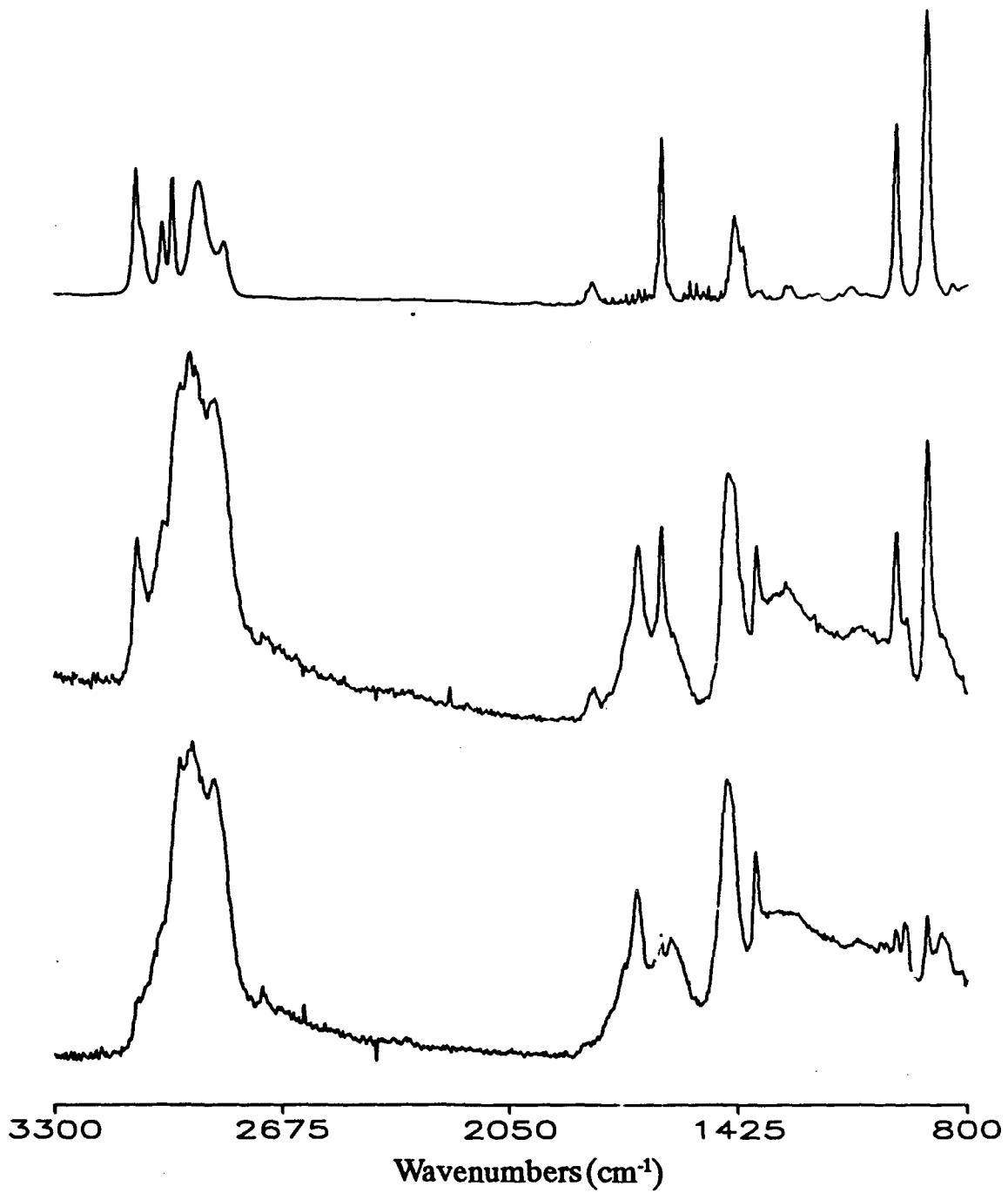
mathias Fig 5



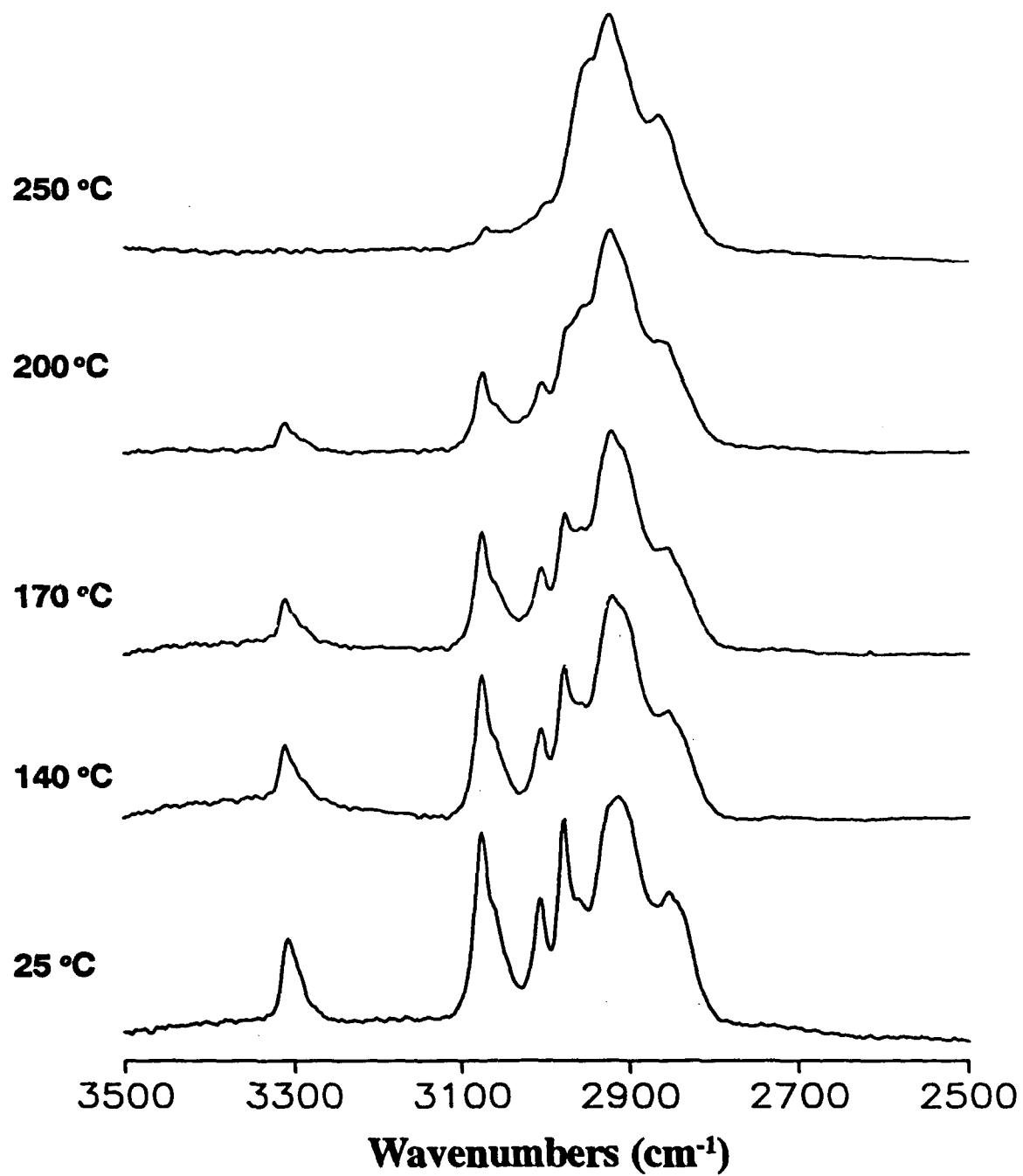
Marshas Fig 6



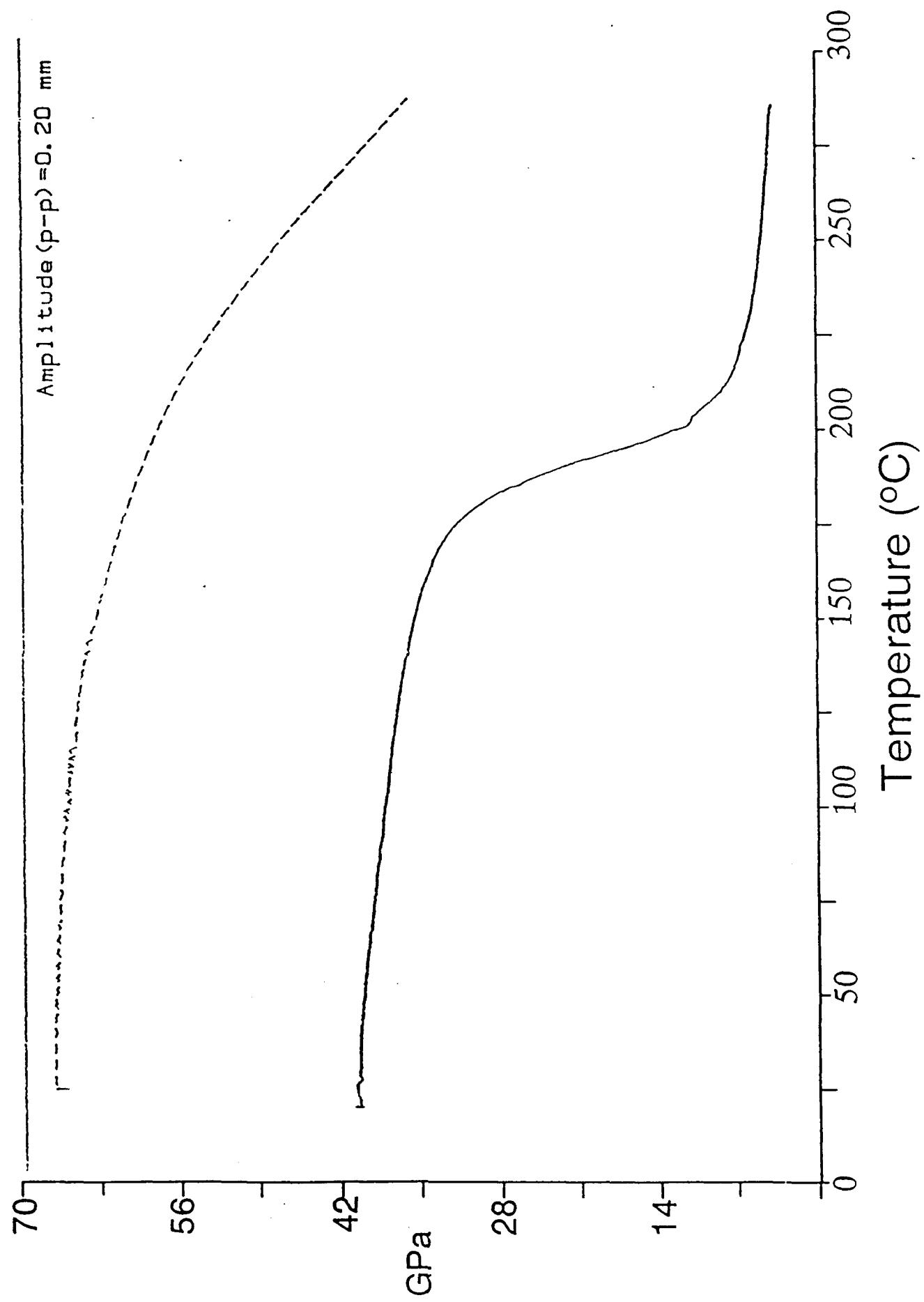
Mathias Fig 7



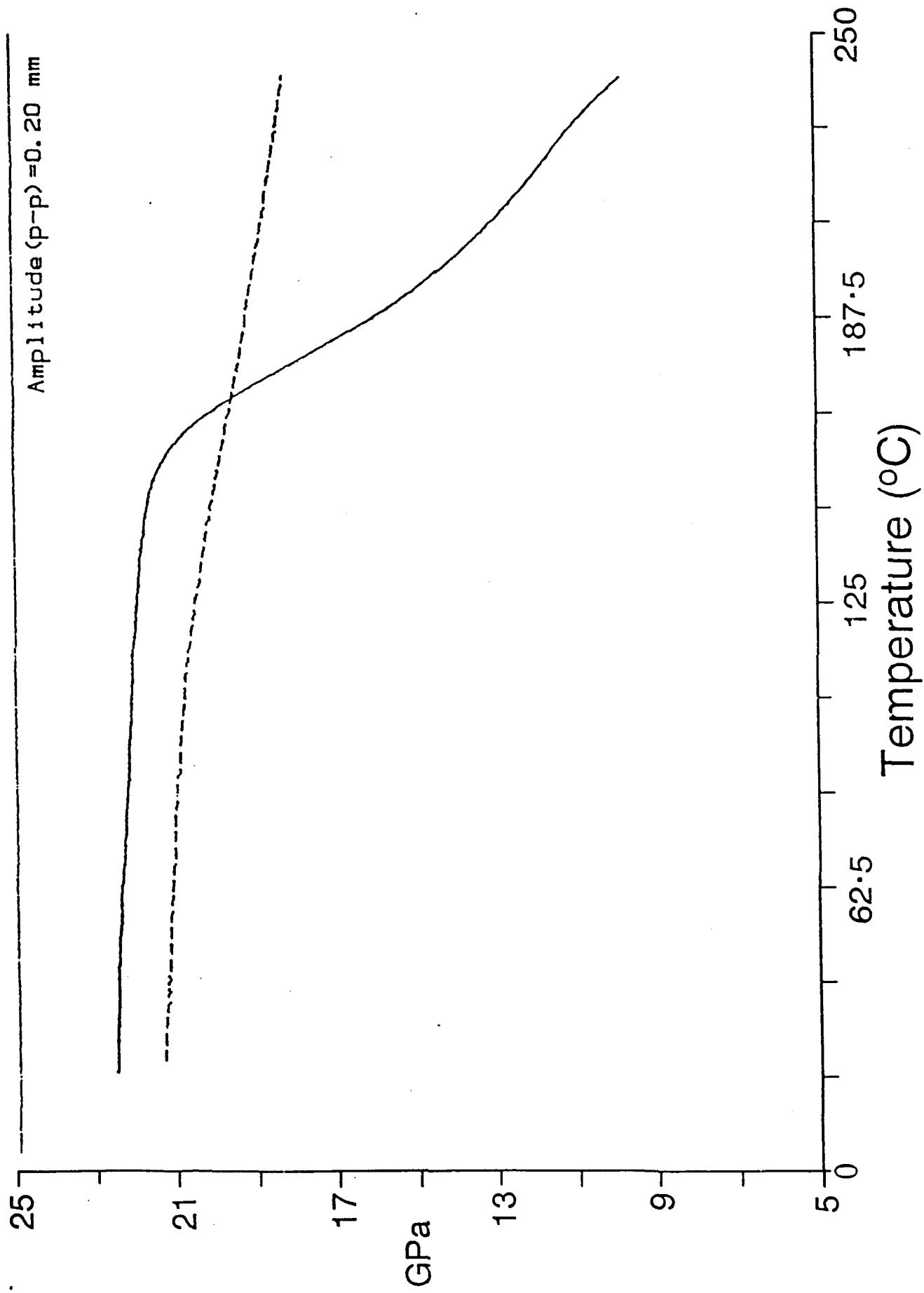
• Rathnas Fig 8



Mathias Fig 9



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Mathias Fig 11

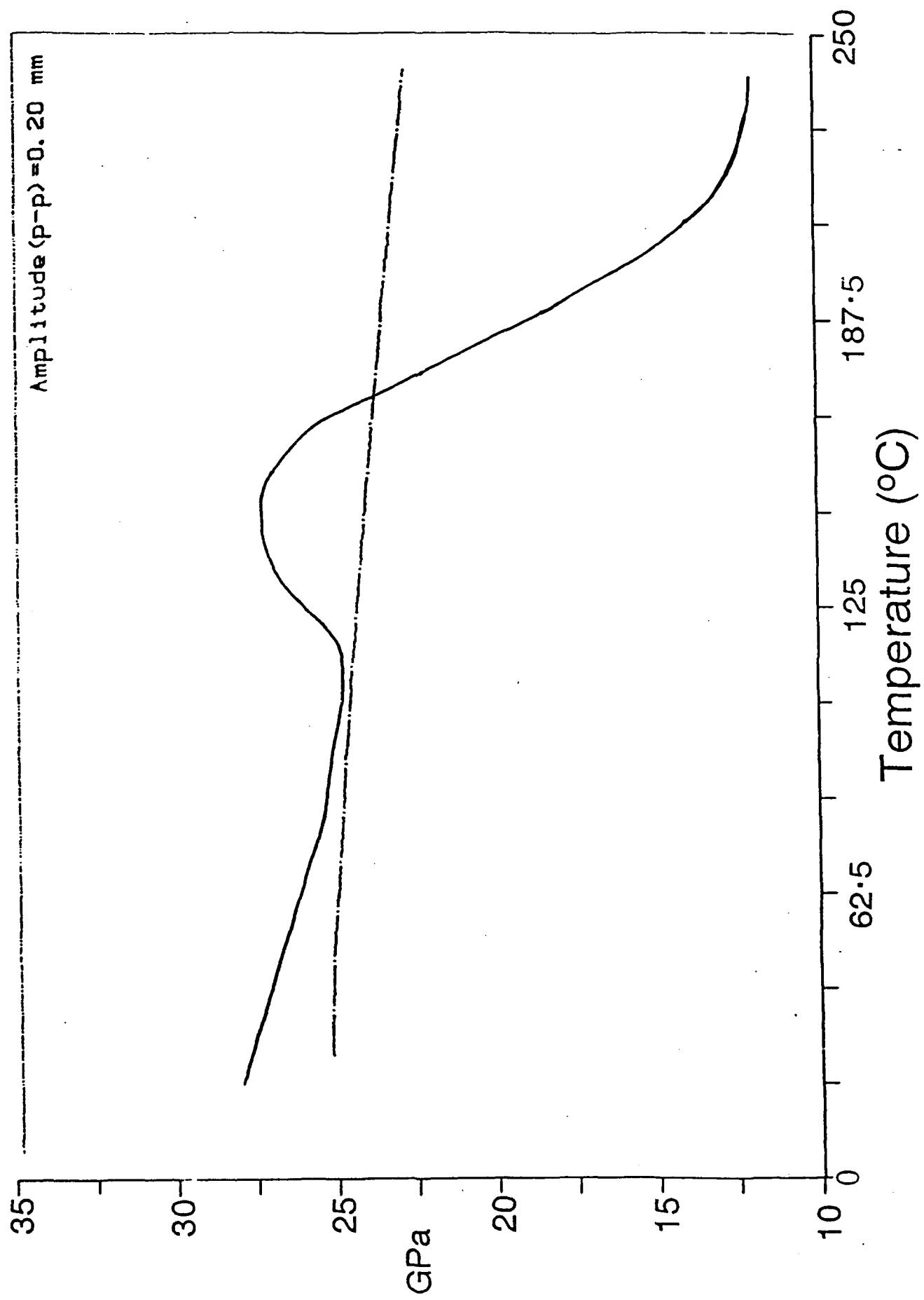
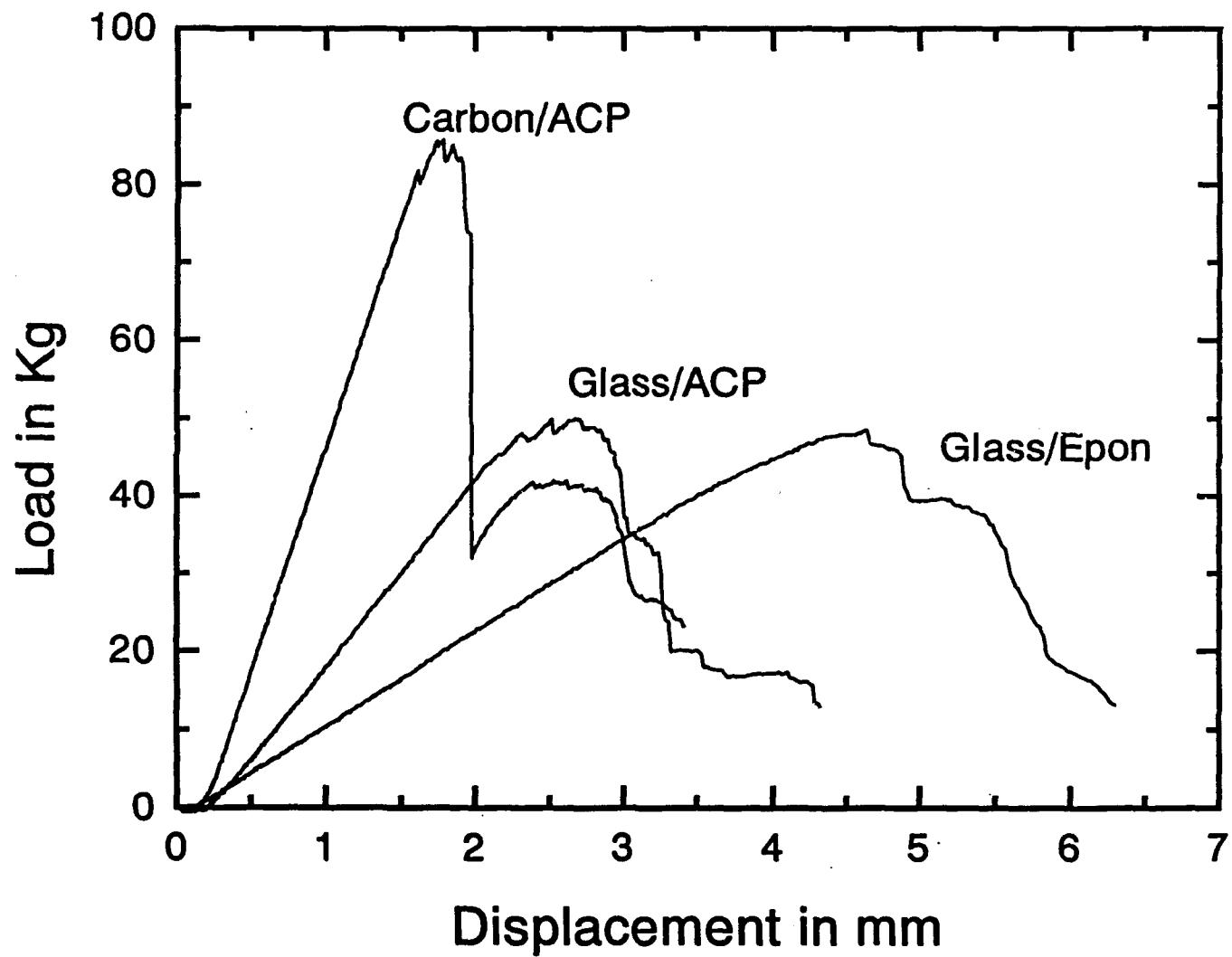


Fig 12, Marheas

Span to thickness ratio = 16  
Strain rate = 2mm/min



Marshas Fig 13

mj 74880 neat resin with untreated carbon fibers

